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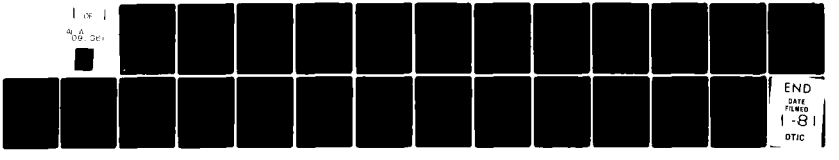

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A QUALITATIVE THEORETICAL CHARACTERIZATION OF HIGH ENERGY EXCITATION CROSS SECTIONS

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An information theoretic approach is used to calculate the cross sections for the vibrational excitation of H_2O and CO_2 by atomic oxygen. The calculational results are shown to compare quite well with existing experimental data.

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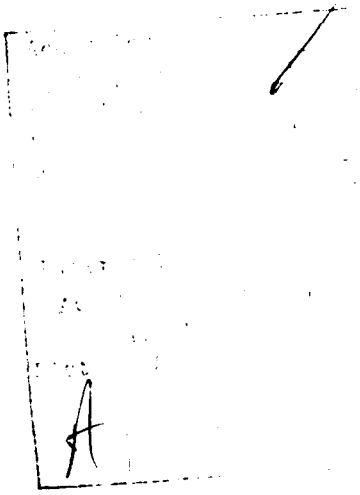

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1. INTRODUCTION

Above 100 km the infrared (IR) radiation from 2 - 50μ emitted from rocket and missile plumes may be produced largely from high velocity molecular collisions between IR-active exhaust-exhaust and exhaust-atmospheric species. At higher altitudes these IR-signatures are dominated by the latter process, the predominant atmospheric species being atomic oxygen. Since these interactions occur with high relative energies, collisions between atomic oxygen and exhaust species such as HF, H_2O, and CO_2 may result in excitation, reaction, or dissociation processes. In the present work we will be concerned only with nonreactive excitation processes.

At present, laboratory data exists only for vibrational excitation of CO_2[1,2] by N_2, O_2 and Ar and H_2O[3] by N_2. There has been one field measurement of a high altitude infrared exhaust plume signature from which an excitation cross section for H_2O and CO_2 (by O-atoms) has been extracted.[4] Due to the complexity, the only theoretical work[5] on the vibrational excitation of CO_2 by O has considered CO_2 as a diatomic molecule.

The present work represents an initial study of the theoretical characterization of excitation cross sections of H_2O and CO_2 in collisions with a structureless particle, i.e.,

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(1) Subbarao, R., Fenn, J.B., and Kolb, C.E., J. Chem. Phys. to be submitted.

(2) Rahbee, A., Gibson, J., and Dolan, C., private communication (1980).

(3) Dunn, M.G., Skinner, G.T., and Treamor, C.E., AIAA J. 13, 803 (1975).

(4) McIntyre, A., Gersh, M.E., Wheeler, N.B., Frankel, D.S., and Elgin, J.B., private communication (1979).

(5) Bass, J.N., J. Chem. Phys. 60, 2913 (1974).

$$M + H_2O \longrightarrow M + H_2O^{\ddagger}$$

and

$$M + CO_2 \longrightarrow M + CO_2^{\ddagger}$$

Although a complete study of the dynamics of these processes is needed, it has been shown that the qualitative concepts of the information theoretic approach are quite useful.[6] We show the results of such a study. We find that the energy dependence of these cross sections appears to agree quite well with that from the available experimental results.

The organization of this work is as follows: Section 2 presents a general outline of the theoretical methods used, and Section 3 discusses the predicted excitation cross sections and compares them with existing data.

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(6) For reviews, see (a) Levine, R.D. and Bernstein, R.B., Acc. Chem. Res. 7, 393 (1974); (b) Bernstein, R.B. and Levine, R.D., Adv. At. Mol. Phys. 11, 215 (1975); (c) Levine, R.D. and Bernstein, R.B., in Modern Theoretical Chemistry, Vol. II: Dynamics of Molecular Collisions, ed. by W.H. Miller (Plenum, New York, 1976), p. 323.

2. THEORETICAL METHOD

The information theory approach to dynamics is well documented in the literature[6,7] and will only be outlined here.

The state-to-state cross section for reactants in quantum state n and products in the final state n' is given by[5,6]

$$\sigma(n \to n'; E) = \frac{(2\pi)^4}{g_n k_n^2} \rho_T(E - E_n) \rho_T(E - E_{n'}) |T_{nn'}|^2 \quad (1)$$

where E is the total energy, g_i and E_i are the degeneracy and energy of the i^{th} internal quantum level, $T_{nn'}$ is the transition matrix element for the $n \to n'$ transition, $k_n^2 = 2\mu(E - E_n)/\hbar^2$ with μ as the reduced mass, and $\rho_T(E - E_i)$ is the translational density of states for a species in the i^{th} quantum level, i.e.,

$$\rho_T(E - E_i) = g_i A_T(E - E_i)^{1/2} \quad (2a)$$

with

$$A_T = \mu^{3/2}/2^{1/2}\pi^2\hbar^3 \quad (2b)$$

The concept of a "Prior" cross section, labeled σ^o, is that which obtains when all quantum transitions are taken to be equally probable, i.e.,

$$T_{nn'} = \text{constant} . \quad (3)$$

---

[7] Procaccia, I. and Levine, R.D., J. Chem. Phys. 64, 808 (1976).

Inserting Eqs. (2) and (3) into (1) yields

$$\sigma^{o}(n \to n';\ E) = B\, g_{n'} \left[\frac{E - E_{n'}}{E - E_{n}}\right]^{1/2} \tag{4a}$$

$$= B\, g_{n'} (1 - Q_{nn'}/E_T)^{1/2} \ . \tag{4b}$$

Here, B is a collection of constant factors, the initial translational energy is $E_T = E - E_n$, and the energy defect of the transition, $Q_{nn'}$, is given by

$$Q_{nn'} = (E_{n'} + E_{o'}) - (E_n + E_o) \ . \tag{5}$$

Note that E_n is the internal energy relative to the zero point level (for electronically adiabatic nonreactive processes, $E_o = E_{o'}$). It is interesting that on purely kinematic grounds (i.e., no dynamical considerations), the prior cross section decreases for exoergic ($Q_{nn'} < 0$) processes and increases for endoergic ($Q_{nn'} > 0$) processes.

Now, the true transition cross section will differ from the prior cross section due to various dynamical effects or constraints. It is the goal of information theory to predict the "best" form of the cross section consistent with the observables of the process. This is accomplished by use of the Maximum Entropy Principle,[6] which simply stated means that a system proceeds such that the entropy achieves its maximal allowed value, constrained of course, to reproduce the independent observables.

Now, the state-to-state cross section may be written in the form

$$\sigma(n \to n') = \sigma(n)\, P(n'|n) \tag{6}$$

where $\sigma(n)$ is the total cross section out of state n and $P(n'|n)$ is the conditional probability of scattering into state n' given a reactant in state n, namely

$$P(n'|n) = \frac{\sigma(n \to n')}{\sum_{n'} \sigma(n \to n')} \tag{7}$$

If there were only one independent observable, say the average of the variable x, then the Maximum Entropy Principle would predict the form[6,7]

$$P(n'|n) = P^{o}(n'|n) \exp(-\lambda_o - \lambda x) , \tag{8}$$

where λ_o and λ are Lagrange multipliers. $P^{o}(n'|n)$ may be obtained via Eq. (7) with σ replaced by σ^{o}.

For the present, we assume that in an inelastic collision process there is only one independent observable which is the average absolute fractional energy transferred. That is,

$$x = |f_{n'} - f_n| = |\Delta f|$$

with

$$f_n = E_n/E, \tag{9}$$

and therefore,

$$\sigma(n \to n') = A \frac{\sigma^{o}(n \to n') e^{-\lambda|\Delta f|}}{\sum_{n'} \sigma^{o}(n \to n')} \tag{10}$$

where $A = \sigma(n) \exp(-\lambda_o)$. Of the two unknown constants in Eq. (10), A and λ, typically A is a slowly varying function of energy and the majority of the energy dependence of σ is contained in λ. We assume A to be independent of energy. The parameter λ will be determined by a procedure known as the Sum Rule.[7]

The concept of the Sum Rule is as follows: The average fractional energy transferred from an initial state n is given by

$$\langle \Delta f \rangle = \sum_{n'} \Delta f \, P(n'|n) \, . \tag{11}$$

Now when n is the lowest state, $E_{n'} \geq E_n$ for all n' and thus $\langle \Delta f \rangle \geq 0$. Here the system tends to gain energy per collision. When n is the highest state allowed for the given E, $E_{n'} < E_n$ for all n' and thus $\langle \Delta f \rangle < 0$ and the system tends to lose energy per collision. Clearly, for some n, say $\tilde{n}$ (perhaps not integral), $\langle \Delta f \rangle = 0$. That is, when the initial energy is $E_{\tilde{n}}$, the average energy transferred is zero, the system neither tends to gain nor lose energy per collision. Following the lead of Procaccia and Levine,[7] we assume that $E_{\tilde{n}}$ is the microcannonical equilibrium value corresponding to an average over $E_n^{1/2}$, namely

$$E_{\tilde{n}} \equiv \left[\sum_n E_n^{1/2} \, f(n|E) \right]^2 \tag{12a}$$

where

$$f(n|E) = (E - E_n) \, g_n / \sum_n (E - E_n) g_n \, . \tag{12b}$$

Therefore, using Eqs. (4-12), $\lambda(E)$ is obtained from the solution of

$$0 \equiv \sum_{n'} \Delta f \, g_{n'} (E - E_{n'})^{1/2} \, e^{-\lambda |\Delta f|} \tag{13}$$

When there are two degrees of freedom, say n_1 and n_2, then the probability of energy transfer from $n_1 n_2$ to $n_1' n_2'$ may be written as

$$P(n_1' n_2' | n_1 n_2) = P(n_1' | n_1 n_2) \, P(n_2' | n_1' n_1 n_2) \tag{14}$$

where the second term is the probability of ending in n_2' given a particular n_1'. The first term is simply

$$P(n_1'|n_1n_2) = \sum_{n_2'} P(n_1'n_2'|n_1n_2) \ . \tag{15}$$

The energy transfer variables corresponding to this division are

$$\Delta f_1 = \frac{E_{n_1'}}{E} - \frac{E_{n_1}}{E} \tag{16a}$$

and

$$\Delta f_2 = \frac{E_{n_2'}}{E - E_{n_1'}} - \frac{E_{n_2}}{E - E_{n_1}} \ . \tag{16b}$$

Thus Δf_1 is the fractional energy transferred to the n_1 degree of freedom and Δf_2 is the fractional energy transferred to the n_2 degree of freedom given the n_1 initial and final states.

The state-to-state cross section is then given by

$$\sigma(n_1n_2 \to n_1'n_2') = \sigma(n_1n_2)\ P(n_1'n_2'|n_1n_2)$$

$$= A\ \frac{g_{n_1'}g_{n_2'}(E - E_{n_1'} - E_{n_2'})^{1/2}\ e^{-\lambda_1|\Delta f_1| - \lambda_2|\Delta f_2|}}{\sum_{n_1'n_2'} g_{n_1'}g_{n_2'}(E - E_{n_1'} - E_{n_2'})^{1/2}} \tag{17}$$

Corresponding Sum Rules are given by

$$0 = \sum_{n_1'} \Delta f_1 \, P(n_1' | \tilde{n}_1 \tilde{n}_2)$$

$$= \sum_{n_1'} \sum_{n_2'} \Delta f_1 \, g_{n_1'} g_{n_2'} (E - E_{n_1'} - E_{n_2'})^{1/2} \, e^{-\lambda_1 |\Delta f_1|} \qquad (18)$$

and

$$0 = \sum_{n_1'} P(n_1' | \tilde{n}_1 \tilde{n}_2) \sum_{n_2'} \Delta f_2 \, P(n_2' | n_1' \tilde{n}_1 \tilde{n}_2)$$

$$= \sum_{n_1'} \sum_{n_2'} \Delta f_2 \, g_{n_1'} g_{n_2'} (E - E_{n_1'} - E_{n_2'})^{1/2} \, e^{-\lambda_1 |\Delta f_1| - \lambda_2 |\Delta f_2|} . \qquad (19)$$

In Eqs. (18) and (19),

$$\Delta f_1 = \frac{E_{n_1'}}{E} - \frac{E_{\tilde{n}_1}}{E} \qquad (20a)$$

and

$$\Delta f_2 = \frac{E_{n_2'}}{E - E_{n_1}} - \frac{E_{\tilde{n}_2}}{E - E_{\tilde{n}_1}} . \qquad (20b)$$

The generalization to an arbitrary number of degrees of freedom is straightforward and will not be presented here.

3. EXCITATION CROSS SECTIONS

The only information needed to apply the method of Section 2 to a particular system is a model for the energy levels. For the present treatment we will uncouple all vibrational modes. Moreover, due to the computational time involved in molecules such as CO_2 and H_2O with many internal degrees of freedom, we will assume that hot bands do not play a role in the resulting spectra. That is, the ν_1 and ν_2 modes are adiabatic with respect to ν_3 excitation. As will be seen at least for CO_2, this is not a severe limitation. It should be noted, however, that the present treatment may be extended to include all degrees of freedom. Our model is in effect placing additional constraints on the system.

The energy level scheme adopted for CO_2 is

$$E_{\nu_3} = \omega_3(\nu + \tfrac{1}{2}) + \omega_3 x_{33}(\nu + \tfrac{1}{2})^2 \quad , \tag{21a}$$

$$E_j = B_e\, j(j + 1) \quad , \tag{21b}$$

and for H_2O

$$E_{\nu_3} = \omega_3\,(\nu + \tfrac{1}{2}) + \omega_3 x_{33}(\nu + \tfrac{1}{2})^2 \tag{22a}$$

$$E_j = \tfrac{1}{2}(B_e + C_e)\, j(j + 1) \; . \tag{22b}$$

The spectral constants used are given in Table I.

TABLE 1 - SPECTRAL COEFFICIENTS[(a)] FOR CO_2 AND H_2O

	CO_2	H_2O
ω_3	2396.4	3935.6
x_{33}	- 12.63	- 46.37
B_e	0.39163	14.575
C_e	—	9.499

[(a)] Energies in Units of cm^{-1}.

Employing Eqs. (18) and (19), λ_v and λ_j may be obtained for CO_2 and H_2O. These values are given in Figs. 1 and 2. Total ν_3 cross sections are obtained by summing over final rotational states, i.e.,

$$\sigma(\nu_3') \equiv \sigma(0,\ 0,\ 0,\ 0 \to 0,\ 0,\ \nu_3')$$

$$= \sum_{j'} \sigma(0,\ 0,\ 0,\ 0 \to 0,\ 0,\ \nu_3',\ j') \tag{23}$$

A total photon yield cross section may be obtained by

$$\sigma_p = \sum_{\nu_3'} \nu_3' \sigma(\nu_3') \tag{24}$$

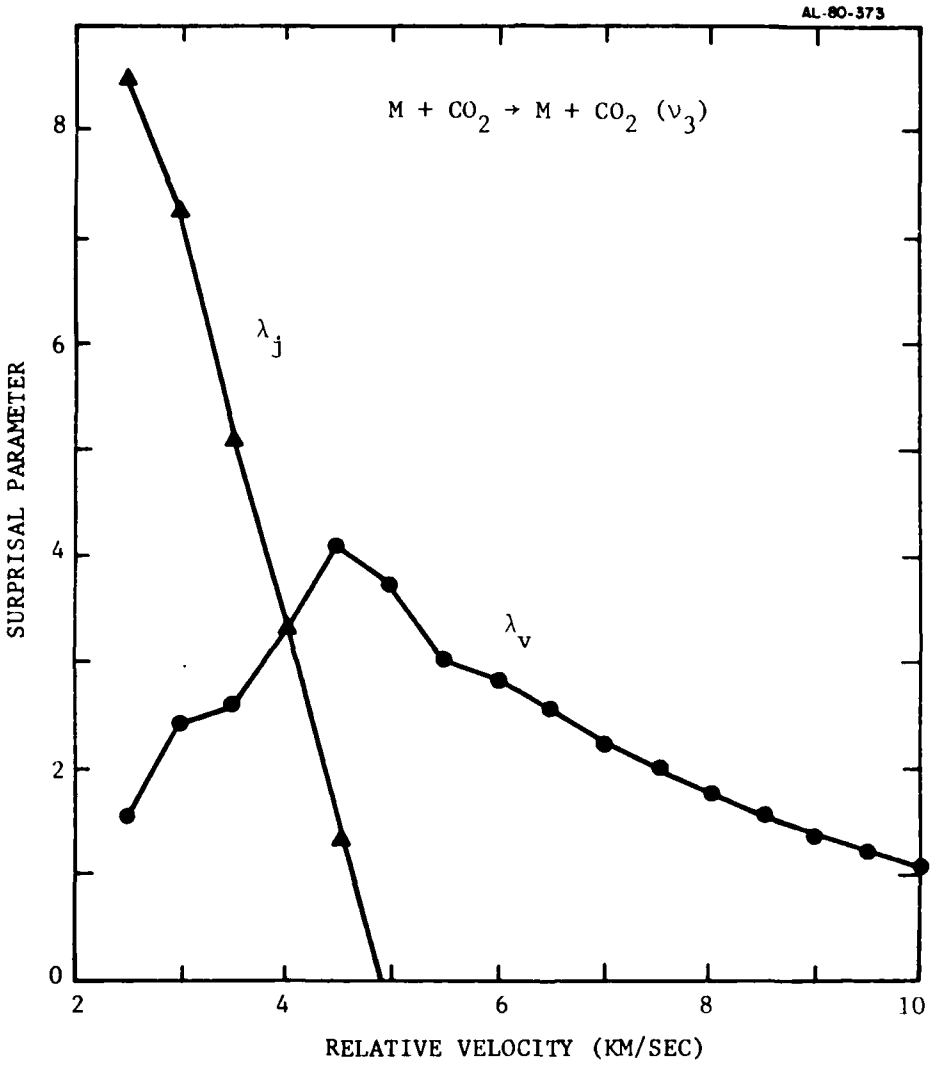

Figure 1. Plot of the CO_2 Surprisal Parameters (Lagrange Multipliers) vs Relative Velocity.

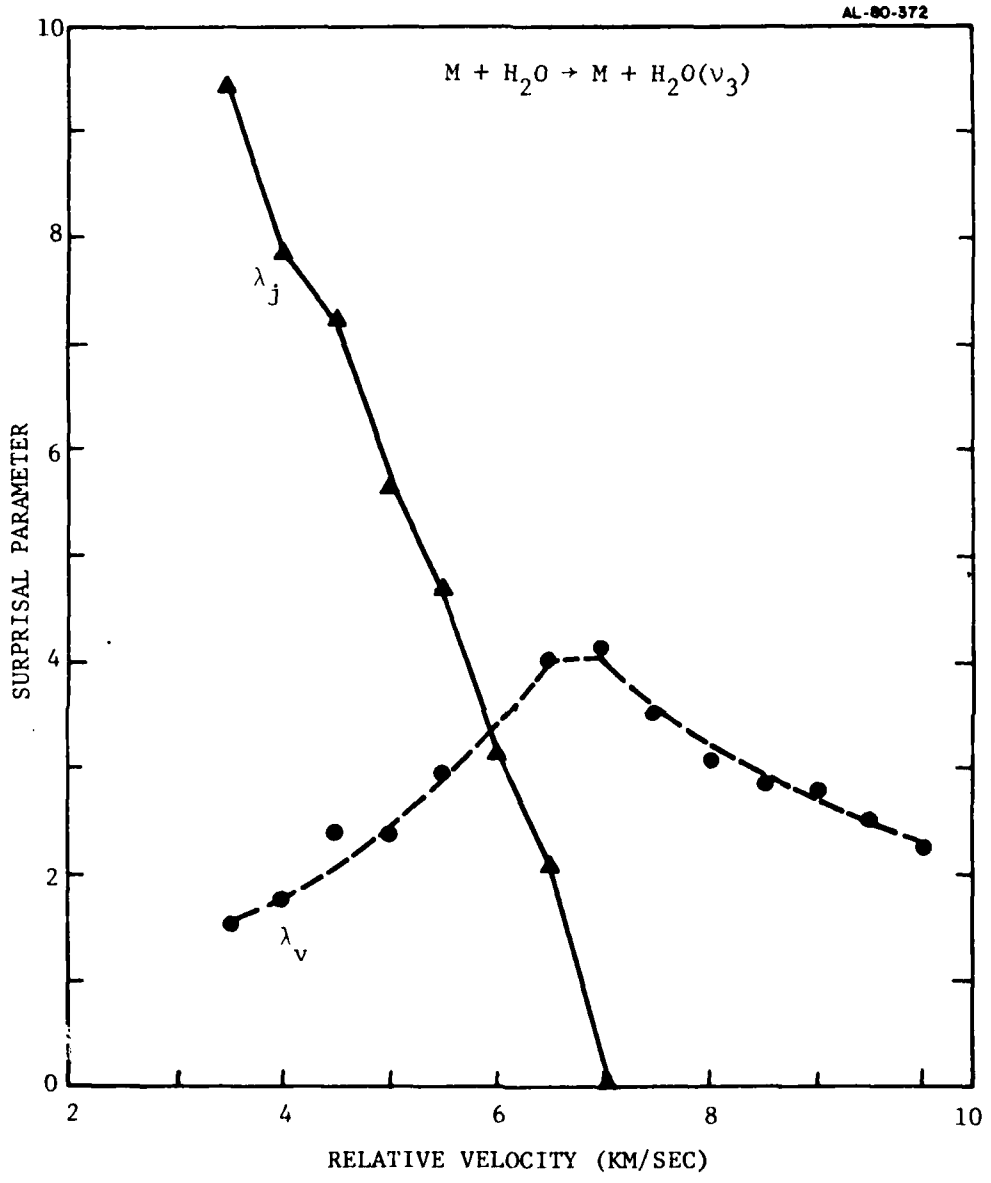

Figure 2. Plot of the H_2O Surprisal Parameters (Lagrange Multipliers) vs Relative Velocity.

This quantity is of prime interest in the plume signature since at high altitudes the meanfree path is long enough to ensure complete radiative relaxation.

Figures 3 and 4 show plots of the calculated energy dependent cross sections. Solid and dashed lines show an arbitrary smoothing in regions which seem unphysical. The magnitude of the present cross sections were chosen to agree with experimental values [1,3] at relative velocities shown by vertical arrow. Unfortunately, H_2O excitation cross sections have only been obtained at one relative velocity eliminating further comparison at this time. The curves labeled "PREVIOUS σ_p" represent cross sections obtained by the author using a less exact treatment.[8] These previous results have been superseded by the present cross sections.

Experimental CO_2 excitation cross sections are better known. Subbarao et al.[1] have measured what are probably $(0 \rightarrow 1)$ absolute excitation cross sections and Rahbee et al.[2] have measured relative $(0 \rightarrow 1)$ excitation cross sections. Figure 5 shows a log σ vs. E comparison of the present calculation with the Subbarao et al. data (points). Open circles indicate less accurate data. All experimental data is shown for comparison on a linear plot in Fig. 6. It is noted that σ_p seems to be a better fit to the data. However, the experimental configuration is such that at most one photon per excitation collision may be detected.

In conclusion, it should be noted that the theory presented here extends the current literature and thus more research is necessary (both experimental and theoretical) to understand any restrictions which must be considered. However, these results are certainly encouraging.

---

[8] Gersh, M.E., Elgin, J., Faist, M., and Bernstein, L.S., "High Altitude Rocket Plume Radiation Calculations," Presented at AFGL High Altitude Plume Workshop, Hanscom AFB, MA (1978).

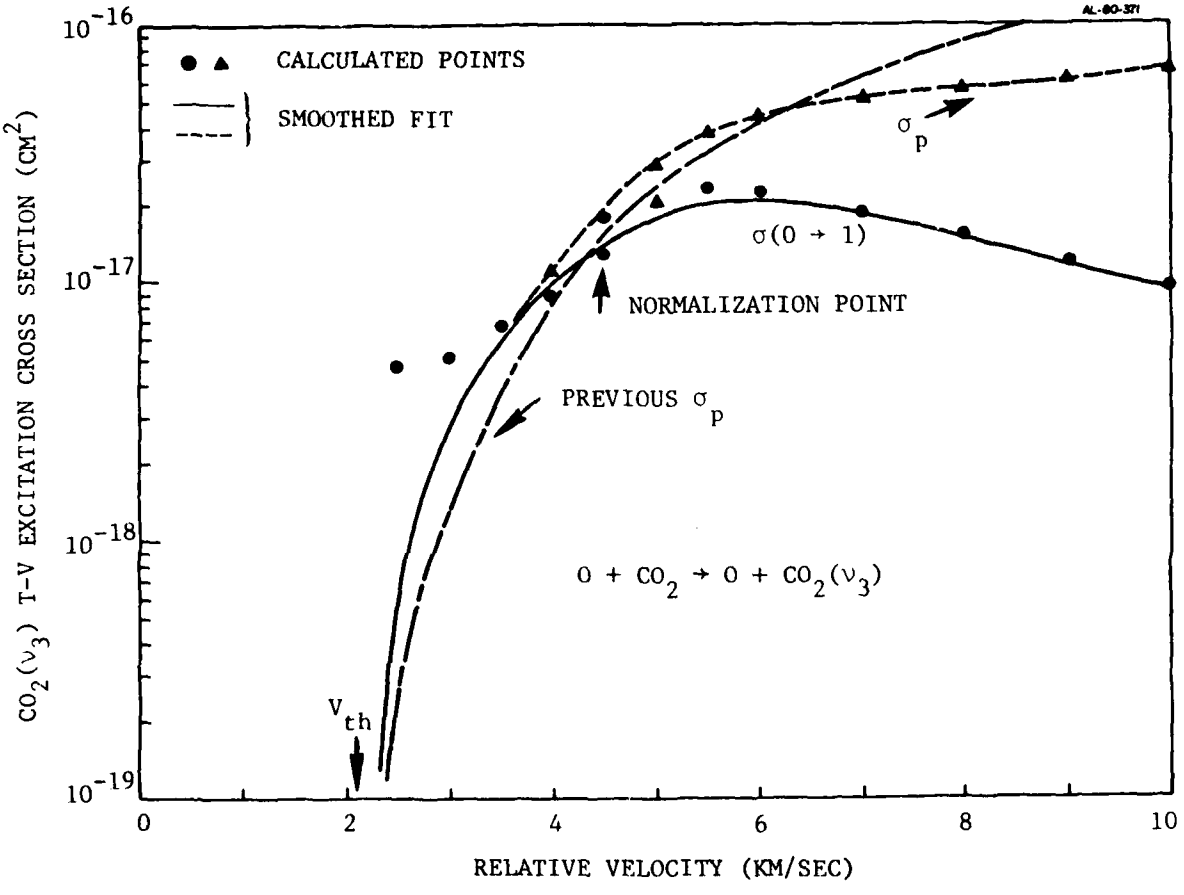

Figure 3. Calculated Energy Dependent Cross Sections for CO_2.

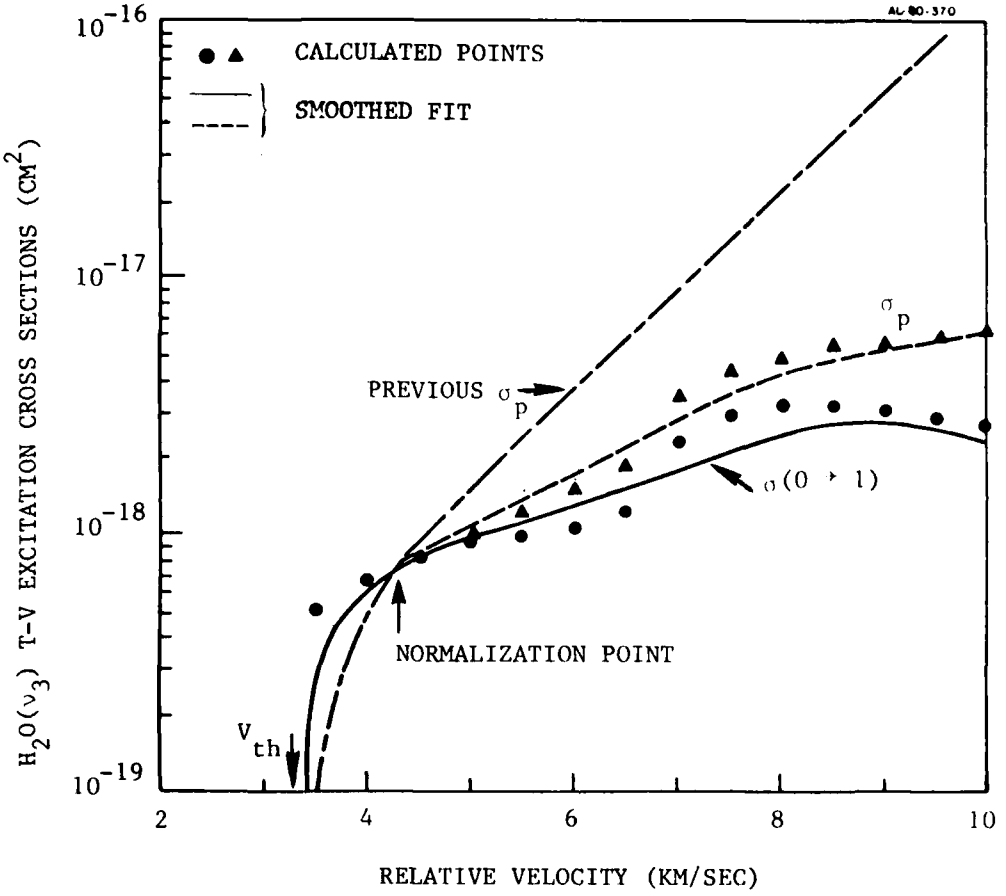

Figure 4. Calculated Energy Dependent Cross Sections for H_2O.

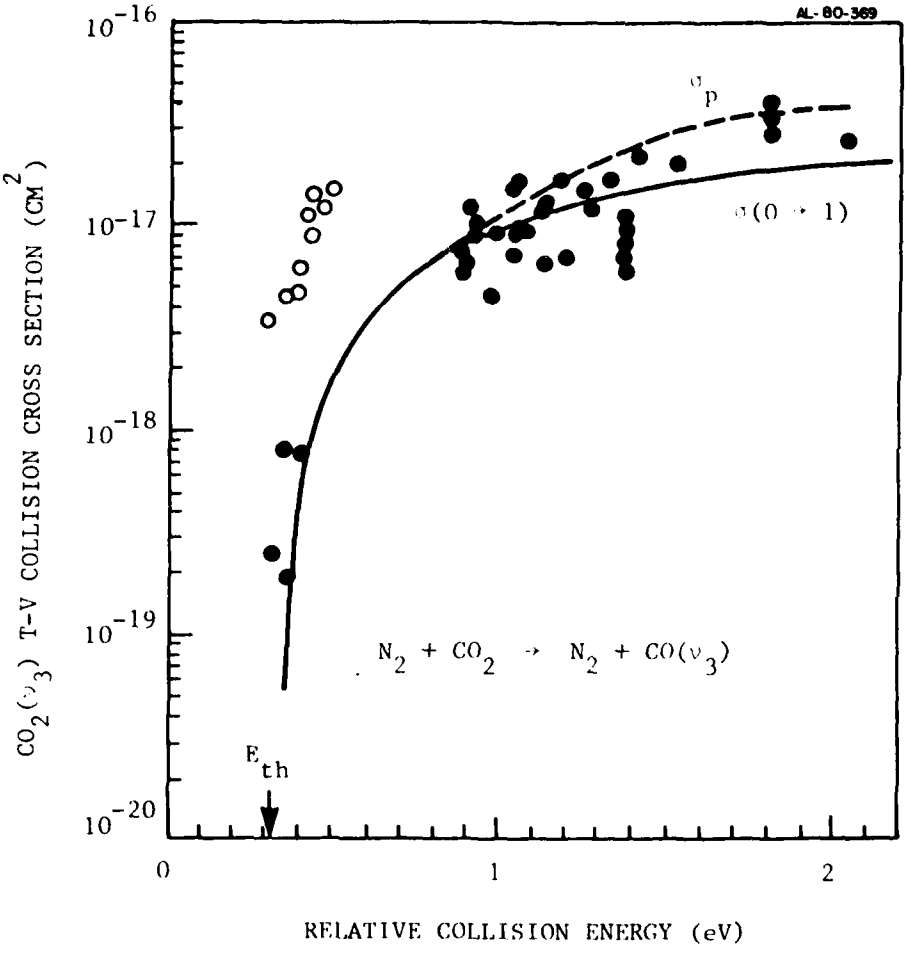

Figure 5. Comparison of Present Calculation with Data of Subbarao et al[1]

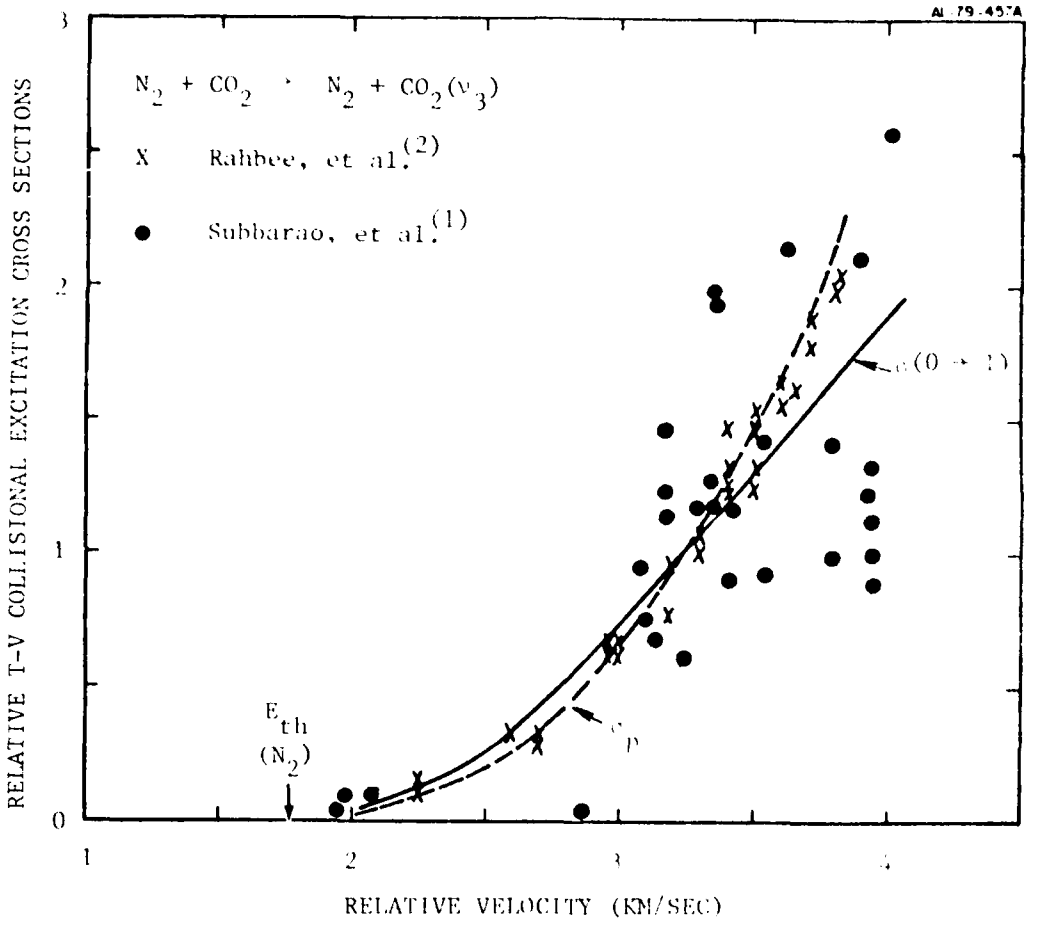

Figure 6. Comparison of Present Calculation with Data of Subbarao, et al.(1) and Rahbee, et al.(2)

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4. McIntyre, A., Gersh, M.E., Wheeler, N.B., Frankel, D.S., and Elgin, J.B., private communication (1979)

5. Bass, J.N., J. Chem. Phys. 60, 2913 (1974).

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7. Procaccia, I. and Levine, R.D., J. Chem. Phys. 64, 808 (1976).

8. Gersh, M.E., Elgin, J., Faist, M., and Bernstein, L.S., "High Altitude Rocket Plume Radiation Calculations," Presented at AFGL High Altitude Plume Workshop, Hanscom AFB, MA (1978).